Absence of spin gap in the superconducting ladder compound $Sr_2Ca_{12}Cu_{24}O_{41}$

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Transport and ^{63}Cu-NMR, Knight shift and T_1, measurements performed on the two-leg spin ladders of $Sr_2Ca_{12}Cu_{24}O_{41}$ single crystals show a collapse of the gap in ladder spin excitations when superconductivity is stabilised under a pressure of 29 kbar. These results support the prediction made with exact diagonalisation techniques in two-leg isotropic t-J ladders of a transition between a low-doping spin gap phase and a gapless 1-D Tomonaga-Luttinger regime.

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I. INTRODUCTION

The existence of superconductivity in two families of materials where this property was not expected at first sight (the low dimensional organic conductors and the high T_c cuprates) has been a major achievement of condensed matter research of the last two decades. The mechanism of superconductivity for both classes of compounds is still under intense debate but there is already a consensus about their low dimensional electronic structure which may be the clue governing superconducting pairing correlations. The recent finding of new superconducting copper-oxide structures [1] exhibiting one dimensional features with both isolated CuO_2 chains and Cu_2O_3 ladders, that is, pairs of CuO_2 chains linked by oxygen atoms between the coppers, has profoundly revived the interest for superconductivity in cuprates and 1-D materials.

The ladder compound to be discussed in this report is $Sr_2Ca_{12}Cu_{24}O_{41}$ which derives from the parent compound $Sr_{14}Cu_{24}O_{41}$ through covalent-calcium substitution. The structure of $Sr_{14}Cu_{24}O_{41}$ displays together CuO_2 chains and Cu_2O_3 two-leg ladders parallel to the c-axis of the structure [2]. Note that other insulating 1-D materials like $SrCu_2O_3$ contain only Cu_2O_3 ladders and no chain. In contrast, the undoped parent compound for the high T_c cuprates exhibits a two dimensional (2-D) CuO_2 layer structure. In both systems, all copper sites belonging to the ladders or to the planes are occupied by a spin 1/2 Cu^{2+} ion. However, while long range antiferromagnetism is stabilized at low temperature in the 2-D spin system, the properties of the spin ladder materials can be drastically different. In two-leg ladders systems,

dominant AF coupling J between the copper spins on the same rung leads to the formation of a spin singlet on each rung. Consequently the ground state of the whole ladder is a singlet spin state with a finite energy needed to excite a rung spin singlet to a spin triplet state. A spin gap situation is obtained and can be seen via the exponential drop of the spin susceptibility upon cooling down.

The existence of a spin gap in a spin-ladder structure has been first proposed theoretically [3] and found experimentally in several even-leg ladder copper oxide systems ($SrCu_2O_3$ [4,5], $LaCuO_{2.5}$ [6]) or organic materials [7]. The spin gap is expected to be quite robust to various perturbations. For example, it is predicted to be stable up to arbitrary small magnetic coupling along the rungs of the ladders [8] or in the presence of a small inter-ladder coupling [9].

The persistence of the spin gap upon light hole doping has been established by various techniques (see e.g. Refs. [3,10–12]). Even more exciting was the suggestion that the spin gap leads to an attractive interaction [3,10] of holes on the same rung, hence providing dominant d-wave like superconducting pairing correlations [13,14] which could possibly materialize into a three-dimensional superconducting state at low temperature. In addition, the numerical investigation of the complete phase diagram [15] of the two-leg isotropic $t - J$ ladder (in this model the motion of the Cu^{3+} singlet holes are described by a hopping matrix element t) suggests the possibility of a transition from the low doping spin gap phase (with the concomitant formation of hole pairs) towards a gapless 1-D Tomonaga-Luttinger (TL) regime. Although, the existence of such a transition is clear at sufficiently

large doping (where, like in the non-interacting picture, the bonding band only becomes relevant), there are some indications that such a TL phase might also be stable at small doping and small J/t ratio (typically around $J/t \sim 0.2$ for a hole concentration of 0.2 hole per ladder-Cu).

Some similarities between the superconductivity in Q-1-D organic conductors [16] and in ladder copper oxides have been noted [17] since, for both cases, superconductivity arises once a charge localized state is suppressed above a critical pressure. The resemblance has to be taken "cum grano salis" since the band filling is exactly one half in organic conductors whereas it is definitely different from one half and possibly pressure-dependent, in the case of ladders. Furthermore, the localization process is due to the existence of a spin density wave state in organics [16] while it can be attributed to a charge density wave state in ladder compounds.

Optical conductivity measurements of $Sr_{14-x}Ca_xCu_{24}O_{41}$ have shown that holes are transferred to the ladders from the chains upon increasing the Ca concentration [18] . A copper valency of ~ 2.2 is therefore reached in $Sr_2Ca_{12}Cu_{24}O_{41}$ (hole density of 0.2 per ladder-Cu). What pressure might do is to further increase the density of holes in ladder-Cu and/or possibly decrease the ratio J/t and trigger the transition from the spin gap regime to a TL regime with low-lying spin excitations.

The prediction of a coexistence, in the lightly doped regime, of the spin gap with divergent superconducting correlations [13] is very suggestive for experimentalists. Therefore, it is a crucial experimental test to investigate whether the finite spin gap persists in spin excitations of $Sr_{14-x}Ca_xCu_{24}O_{41}$ when superconductivity of Ca-substituted compounds is stabilized under pressure. We present the preliminary results of transport and ^{63}Cu-NMR studies performed on a $Sr_2Ca_{12}Cu_{24}O_{41}$ single crystal under pressure. We show, at 30 kbar, the simultaneous onset of superconductivity below 5 K and the existence of low-lying spin excitations from the temperature dependence of the ^{63}Cu Knight shift belonging to the ladders.

II. EXPERIMENTAL RESULTS

The two studies have been carried out on two samples ($(0.75 \times 0.65 \times 1.18)$ mm^3 for transport experiments and $(2.12 \times 0.9 \times 1.12)$ mm^3 for NMR, along a, b and c-axes respectively) cut out from a slice of a monodomain single crystal, several centimeters long, grown by the travelling solvent floating zone method in an infrared image furnace under an oxygen pressure of 13 bar [19].

Transport data have been obtained by a conventional four-contact AC lock-in technique using a non- magnetic high pressure clamped cell. The 73 % increase of the c-axis conductivity at 30 kbar is in fair agreement with the

other single crystal data in the literature [20,21]. Under 26 kbar, ρ_c reveals a metal-like temperature dependence, with a charge localisation beginning around 30 K but no sign of superconductivity above 1.8 K which was our lowest temperature. The metal-like behavior of ρ_c is quite similar under 29 kbar (Fig. 1) but the weak localization at low temperature is stopped at 5 K by a sudden drop of the resistance which compares rather well with the pressure data obtained on a sample which was slightly less hole-doped [21]. We believe that the resistance drop can be confidently ascribed to the onset of a pressure-induced superconducting ground state.
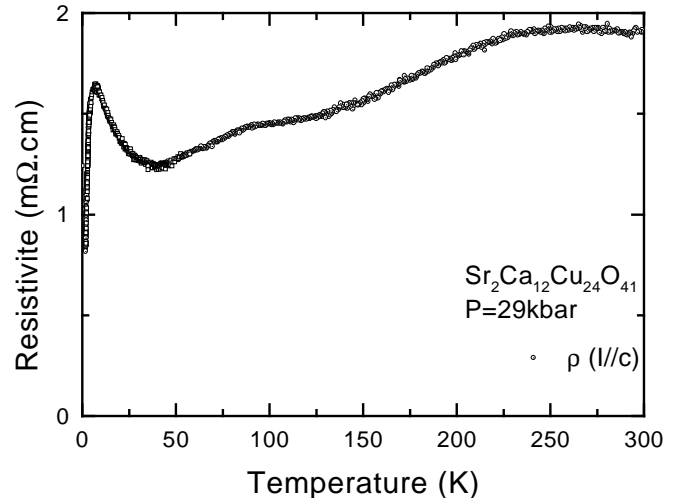

FIG. 1. Temperature dependence of the resistivity along the ladders under 29 kbar. The onset of superconductivity is at 5 K.

The ^{63}Cu-NMR experiments have been performed in the same high pressure cell at an NMR frequency of 87.05 MHz. ^{63}Cu-NMR signals were obtained by recording the spin-echo amplitude of the central transition (1/2, -1/2) of the copper nuclei pertaining to the ladders. A narrow ^{63}Cu-NMR signal has also been obtained by the usual Fourier transform method. It has been attributed to ^{63}Cu nuclei in the pressure cell surrounding the sample. Since the Knight shift of copper metal is known to be insensitive to pressure on the scale of Knight shift variations to be discussed below [22] the narrow signal has been used as a sensitive in-situ magnetic field marker.

Figure 2 presents the temperature dependence of the ^{63}Cu-NMR line position with H//b-axis under 30 kbar and also, in the same pressure cell, after releasing the pressure. The central line position is affected by magnetic shift and by second order quadrupolar shift. We estimate here the latter to be about 300 ppm. Moreover we know that the variation of the quadrupolar frequency with temperature did not exceed 10 % [23]. The scattering of the data at low temperature is due to an increase of the linewidth below 30 K. The magnetic shift consists

usually of a temperature-independent orbital contribution, plus the spin part which follows the uniform susceptibility and can possibly be temperature and pressure-dependent. The ambient pressure curve in Fig. 2 has been obtained by subtraction of a constant contribution (1.36 %) from the total shift. The ambient pressure data lead to $K_{orb} \sim 1.33$ % and $\Delta_{sp} \sim 250$ K, given the expression for the T-dependent part [24]:

$$K_s(T) \sim \frac{1}{\sqrt{T}} \exp\left(-\frac{\Delta_{sp}}{kT}\right),$$

at $kT \ll \Delta_{sp}$. Making the reasonable assumption of a P-independent orbital shift, and a negligeable variation of the quadrupolar contribution, the 30 kbar data in Fig. 2 show only a weak pressure dependence of the spin part at high temperature ($T > 150$ K) which is at variance with the drastic pressure dependence of the spin part observed at low temperature. Fig. 2 reveals the emergence of a zero temperature susceptibility which amounts to 53 % of the room temperature value. Our data at ambient pressure provide a confirmation for the depression of the spin gap upon doping, as previously announced in the Knight shift study of a $Sr_5Ca_9Cu_{24}O_{41}$ single crystal [25] and also from T_1 data in the whole series corresponding to $0 \le x \le 9$ [26]. However, what is remarkable in Fig. 2 is the existence of low lying spin excitations in the compound $Sr_2Ca_{12}Cu_{24}O_{41}$ under a pressure of 30 kbar which is large enough to evidence the onset of superconductivity at 5 K. First, the coincidence between the stabilization of a superconducting ground state and the collapse of the ladder spin gap is a strong argument in favor of superconductivity taking place on the ladders.
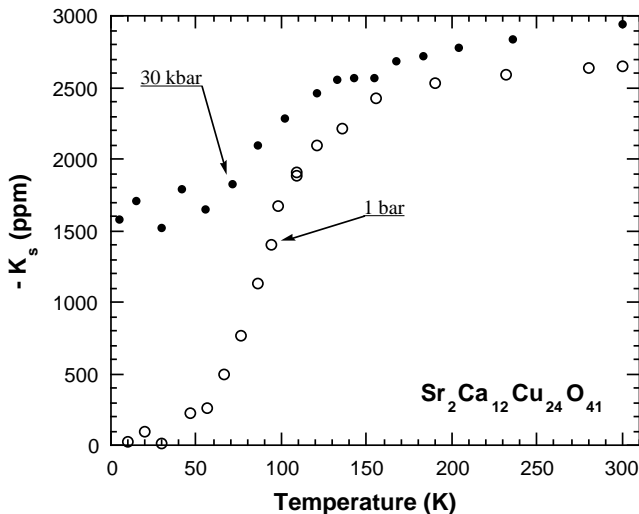

FIG. 2. Temperature dependence of the ^{63}Cu-ladder nuclei Knight shift. A spin gap $\Delta_{sp} \sim 250$ K is obtained from an activation plot below 150K.

Comparing 1 bar and 29 kbar resistivity data we can infer from the smaller increase of the ρ_a/ρ_c anisotropy on cooling at 29 kbar that the confinement of the carriers along the ladders could correlate with the size of the spin gap [27]. This finding suggests a picture of hole pairs being responsible for the conduction within the ladders as long as the magnetic forces can provide the binding of two holes on the same rung [3]. The vanishing of the spin gap could thus be responsible for the dissociation of the pairs, making in turn the hopping of the transverse single particle easier. Secondly, the behavior of the susceptibility under 30 kbar with low-lying spin excitations is at first sight reminiscent of the situation which prevails in quasi 1-D organic conductors where the susceptibility is temperature dependent below 300 K, but noticeably independent of the behavior of the charge degrees of freedom (spin-charge separation in a 1-D chain), which have been understood in terms of a correlated Tomonaga-Luttinger liquid [16].
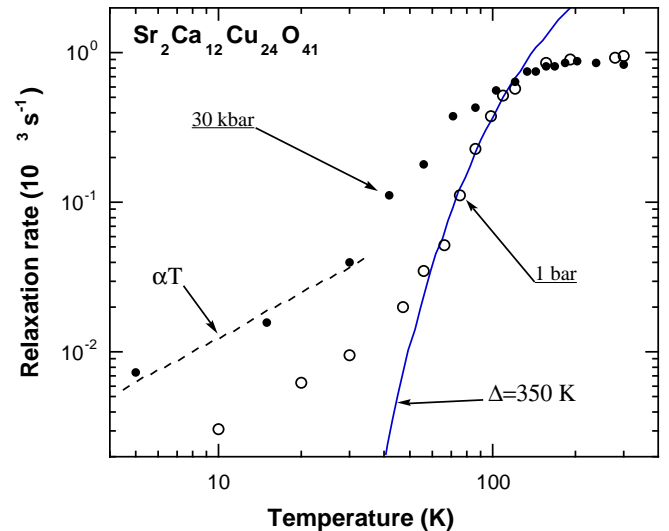

FIG. 3. Temperature dependence of the ^{63}Cu-ladder relaxation rate T_1^{-1} at 1 bar and under 30 kbar.

The nuclear spin lattice relaxation has also been measured since this quantity is known to be a very sensitive probe for the low lying spin excitations in cuprates [28] and 1-D organic conductors [29]. The spin-lattice relaxation with H//b was measured by the saturation-recovery technique and T_1 was determined from the single time constant governing the magnetic relaxation in high field NMR of a quadrupolar nucleus such as ^{63}Cu (I=3/2) [30]. The exponential fit with a single time constant is excellent down to 70 K but is not as good at low temperature and leads to a poorer T_1 determination. The 1 bar and 30 kbar data for $\frac{1}{T_1}$ vs T in logarithmic scales are shown on Fig.3. In the temperature domain 300-200 K, T_1 is both temperature and pressure independent. At 1 bar, T_1 becomes activated below 120 K with an activation energy $\Delta' = 350$ K. This behavior is in fair agree-

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ment with other experiments on single crystals [25]. This activated behavior breaks down below 40 K while under 30 kbar, the relaxation apparently displays quite a different temperature dependence. We can attribute the non activated temperature dependence to the collapsing of the spin gap and the persistence even at low temperature of populated spin excitations modes contributing to the relaxation. At high temperature, however, the absence of significant temperature dependence suggests a relaxation induced by antiferromagnetic fluctuations in Heisenberg chains. In this range of temperature, such a relaxation channel should not be sensitive to the presence or the absence of a spin gap.

III. DISCUSSION

We finish this paper by discussing the above experimental data in the context of existing theoretical work. As stated above, such materials are expected to be accurately described by a two-leg $t - J$ ladder which accounts for the strong nearest-neighbor AF coupling J between the spins and the hole delocalization t. It is believed that, in these materials, interchain and intrachain couplings are quite similar (isotropic case) and comparable in magnitude to their values in the 2-D copper oxide materials (typically $J/t \simeq 0.3 \ldots 0.4$ corresponding to the strong coupling limit). Exact diagonalisation techniques applied to the two-leg $t - J$ ladder have proven, in the isotropic case, the formation of hole pairs at low doping with the concomitant formation of a spin gap [5,10,11], as initially suggested in the anisotropic limit ($J_\perp >> J_\parallel$). A phase diagram for the isotropic $t - J$ ladder as a function of J/t and doping parameters has been established [15] and is schematically shown in Fig. 4. Close to the half-filled band situation, i.e. with a small hole concentration, the spin gapped phase (with a zero energy charge mode) is recovered while a phase with a single gapless spin and a single gapless charge mode is found to become stable under hole doping [11]. Physically, the existence of such a transition can easily be understood from a weakly-interacting band picture [31]. Indeed, for hole density $n_h \geq 0.5$ the higher energy anti-bonding band becomes unoccupied and one recovers a single band picture analogous to the single chain case. However, the line $n_h = 0.5$ is expected to be quite singular since Umklapp scattering characteristic of a half-filled band likely leads to an insulating state [32] and it is not yet clear whether the transition line to the TL phase corresponds precisely to this line. More interestingly, the possiblity of a similar cross-over between the spin gapped phase towards a 1-D TL regime also exists at low doping for a sufficiently small J/t ratio, although it is difficult to estimate numerically the transition line [32] (indicated tentatively in Fig. 4 by a dotted line).

We shall argue here that the experimental data of T_1, together with the loss of susceptibility by a factor about
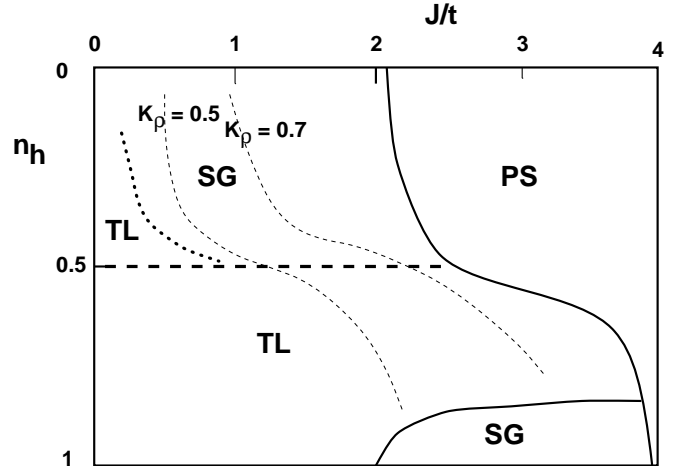

FIG. 4. Schematic phase diagram of the two-leg t-J ladder as a function of J/t and hole density n_h based on exact diagonalisations of small clusters (see Ref. [15]). The thick dashed and dotted lines separate the spin gapped (SG) and Tomonaga-Luttinger (TL) phases. At large unphysical J/t ratios phase separation (PS) occurs. Lines of constant K_ρ (see text) are also indicated (thin dashed lines).

2 could possibly support the existence of such a transition in the $Sr_{14-x}Ca_xCu_{24}O_{41}$ materials, the 1 bar and 29 kbar phases being ascribed to the spin gapped and TL phases respectively. From simple symmetry considerations [11], in a ladder system one expects two spin excitations branches which could independently acquire a gap or be gapless. The exponential decrease of the spin susceptibility at 1 bar (Fig. 2) is characteristic of a full gap in the spin sector. On the other hand, the TL phase exhibits one gapless mode and one mode with a gap. The susceptibility data at 29 kbar are consistent with this scenario. At sufficiently high temperatures both modes are expected to contribute. However, the gapped spin mode is depopulated on decreasing temperature and a pseudo-gap feature can be seen. At the lowest temperatures half of the spin degrees of freedom contribute to the static susceptibility as portrayed by the temperature variation of K_s in Fig. 2.

It is worth looking at the temperature profile of the relaxation rate that would be predicted in the above scenario of the $t - J$ ladder model. First, since for $T > 150K$, T_1^{-1} is found to be temperature independent indicating that antiferromagnetic chain-like spin correlations dominate the relaxation. This suggests that the contribution coming from uniform spin correlations to T_1^{-1} is sufficiently small to be safely ignored for all temperatures and pressures of interest [29]. In the spin gap phase at 1 bar, where both branches of spin excitations are frozen, T_1^{-1} and K_s are thermally activated with slightly different activation energies [25]. At high pressure, however, the restoration of a phase with a gap-

less spin and a gapless charge modes will promote a new channel of relaxation of the TL type. This is well known to introduce a power law component in the temperature dependence of T_1^{-1} which will read

$$T_1^{-1} = C_1 \exp(-\Delta'/k_B T) \; + \; C_2 T^{2K_\rho}$$

in the low temperature domain, where $C_{1,2}$ are positive constants. Here K_ρ stands as the power law exponent of the antiferromagnetic LL response function ($\chi \sim T^{-1+2K_\rho}$) [15]. Since in the metallic phase that is precursor to superconductivity, $2K_\rho$ should be close to unity, it follows that a non thermally activated component sould emerge for T_1^{-1} at sufficiently low temperature. This prediction seems to be in qualitative agreement with the T_1^{-1} data given in Fig. 3. Indeed one finds no thermal activation for the relaxation and this, especially in the temperature range below 50 K where K_s becomes metallic and temperature independent.

In summary, transport and ^{63}Cu-NMR measurements under pressure performed on the prototype $Sr_2Ca_{12}Cu_{24}O_{41}$ doped spin ladder have been reported and analyzed in the context of the t–J ladder model. The drastically different behaviors observed at 1 bar and 29 kbar of the temperature dependence of the local static susceptibility and of the relaxation rate $1/T_1$ are attributed to the appearance of a zero energy spin mode at 29 kbar. We argue that this phase can be identified to the gapless TL metallic phase of the t-J ladder. Since, in the 29 kbar phase, superconductivity sets in at low temperature, this suggests that superconductivity itself might be connected to such a transition and to the collapse of the spin gap. Recent numerical investigations of t–J [33] and Hubbard [14] ladders found that pairing correlations are maximized when the Fermi level lies in a maximum of the density of states, situation which might correspond to the transition discussed in this paper. Clearly more experimental and theoretical work are needed to clarify this important issue.

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